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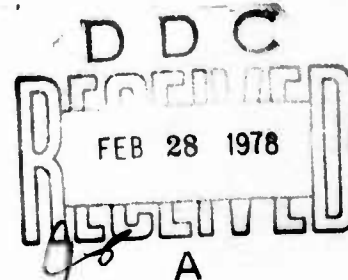
AFML-TR-77-24 ✓

SILOXANE-MODIFIED POLYCARBONATE  
INTERMEDIATES AND MONOMERS

MIDWEST RESEARCH INSTITUTE ✓  
KANSAS CITY, MISSOURI 64110

APRIL 1977

FINAL REPORT FOR PERIOD JANUARY 1976 - DECEMBER 1976



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This technical report covers the work conducted from January 1976-December 1976.

This research was supported by AFML Laboratory Director's Funds.

The work was carried out by Mrs. Cassandra Collins and Mr. Larry Breed who acted as principal investigator.

This technical report has been reviewed and is approved for publication.

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Project Scientist

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Methods of synthesis of intermediates and monomers for the synthesis of siloxane-modified polycarbonates are described. All substances are appropriately characterized. Precursors of polymers with both m-phenylene and p-phenylene moieties as well as precursors of polymers with disiloxanylene, trisiloxanylene, and tetrasiloxanylene groupings are reported.		

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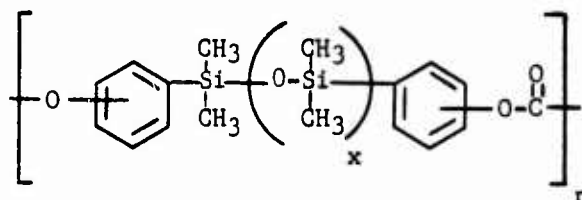


## SECTION I

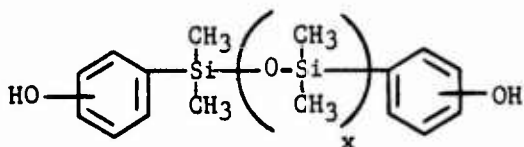
### INTRODUCTION

This report covers work carried out in support of the Air Force effort to develop satisfactory interlayers to be used between plies of polycarbonate and/or glass in aircraft cockpit enclosures. Specifically, it has been concerned with the development of intermediates and monomers which can be converted to suitable siloxane-polycarbonate elastomers to be used in the fabrication of cockpit enclosures with superior impact resistance. Necessary characteristics of the polymers are thermal stability, ultraviolet stability, good low-temperature properties, adhesion to both glass and polycarbonate, good optical properties (no distortion), high light transmission, and low haze.

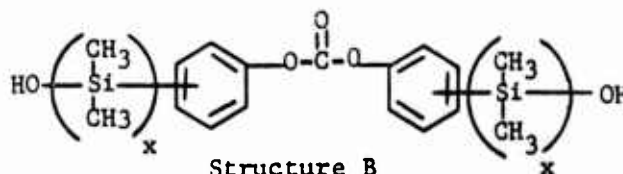
The siloxane-modified polycarbonate polymer selected by the Air Force Materials Laboratory for investigation as a candidate material for this application has the following chemical structure:



Two suitable monomer systems can be proposed for the synthesis of such a polymer: Structure A, which can be polymerized with phosgene in the presence of a base and Structure B, which can be polymerized by dehydration.



Structure A



Structure B

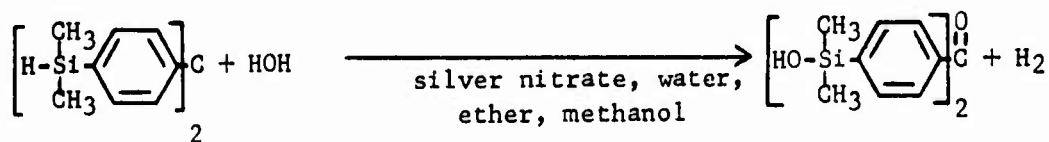
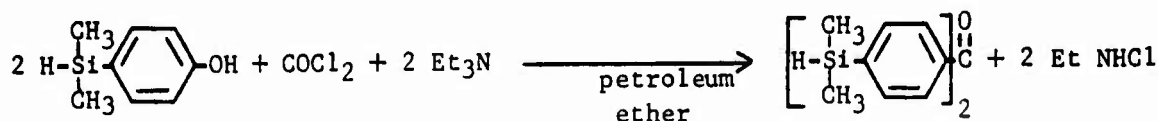
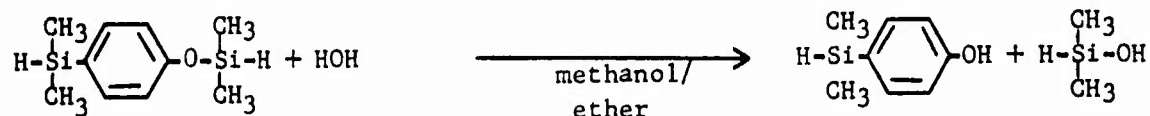
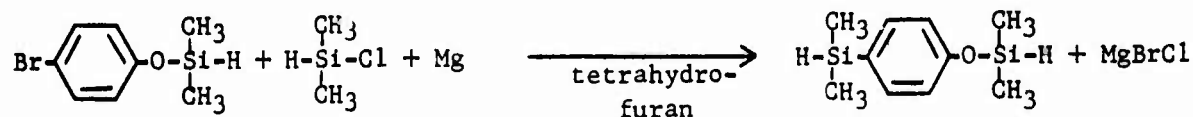
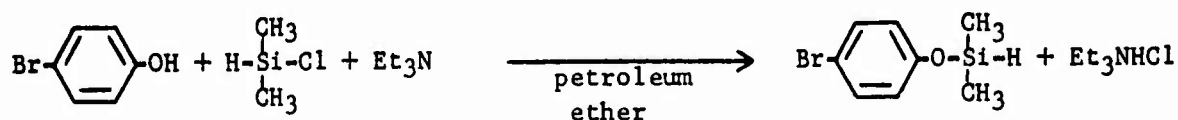
This work encompassed the study of the synthesis of both structures and their intermediates, including compounds with both meta and para substitution and with various values of  $x$ .

## SECTION II

### DISCUSSION

#### 1. Synthesis of Silyl Derivatives of Diphenyl Carbonate

The following sequence of conversions was followed for the preparation of bis(*p*-hydroxydimethylsilylphenyl) carbonate:



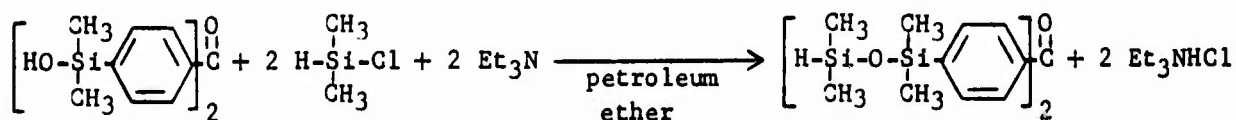
Prior to the formation of a Grignard reagent, the phenolic group was blocked by dimethylsilylation. This group was chosen because of known rearrangements of substituent groups in the course of metallation procedures (Reference 1). The Grignard method described by Neville for the preparation of *p*-trimethylsilylphenoxytrimethylsilane proved satisfactory for the synthesis of *p*-dimethylsilylphenoxydimethylsilane (Reference 2). Although this procedure involved a rather dilute tetrahydrofuran solution of the Grignard reagent, lower yields were obtained in attempts to work with the Grignard reagent at usual concentrations. According to Pearce this compound may also

be prepared by way of the organosodium intermediate by treating *p*-chlorophenyldimethylsilane with chlorodimethylsilane in the presence of sodium (Reference 3). Although the authors reported a 33% yield, the cost of materials could make their procedure attractive for large scale preparations.

The method described by Pearce proved entirely satisfactory for the synthesis of *p*-dimethylsilylphenol (Reference 3), and Lloyd's procedure was satisfactory for preparing bis(*p*-dimethylsilylphenyl) carbonate (Reference 4). More difficulty was encountered in adapting an available method of the synthesis of bis(*p*-hydroxydimethylsilylphenyl) carbonate (Reference 5). A number of variables affected the extent of conversion of the silane group to the silanol group or the by-product siloxane, not all of which were identified. The conversion occurred much more readily and with smaller quantities of silver nitrate reagent at rapid stirring rates, an effect which could be attributed to either the rate of dilution of the reagent or the extent to which the mixture contacted air. More dilute silver nitrate reagent did not seem to affect the course of the reaction; however, a similar procedure under a nitrogen atmosphere resulted in the recovery of unchanged starting material. Therefore, the conversion may well not occur as the silver-catalyzed hydrolysis of the silanic proton shown in the scheme, but rather as a silver-catalyzed oxidation.

According to the nmr spectrum, bis(*p*-hydroxydimethylsilylphenyl) carbonate, m.p. 96 to 97°, obtained by recrystallization from benzene-petroleum ether mixtures was not entirely pure. An unidentified singlet at  $\tau$  2.99 fell within the range of aromatic protons and suggested the possibility of complexed solvent; however, the intensity of the peak was not diminished when samples were heated at 2 hr at 80° under vacuum, conditions under which a solvent would have been removed. Also, there was no evidence by differential thermal analysis of the loss of a volatile component below the melting point.

Bis(*p*-hydroxydimethylsilylphenyl) carbonate was converted to bis(*p*-tetramethyldisiloxanylphenyl) carbonate according to the following scheme:



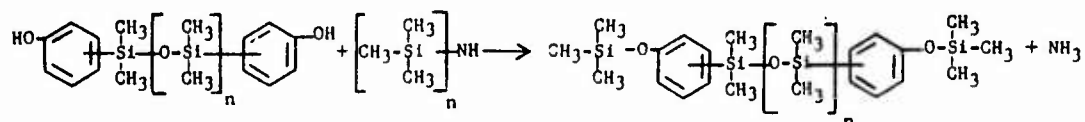
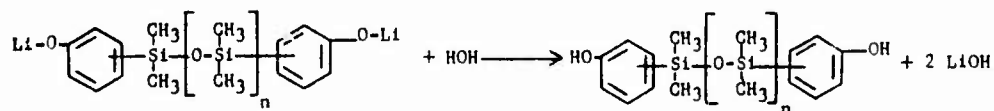
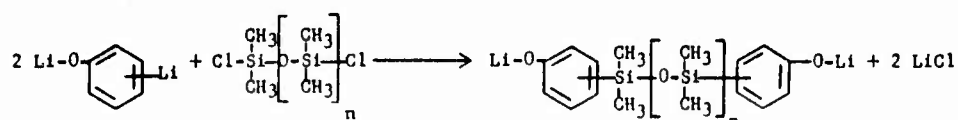
The product could readily be purified by distillation. The same compound treated with diacetyldimethylsilane in the manner described by Korol'ko for the synthesis of structurally related carboranes failed to give a distillable product (Reference 6).



The analogous meta-substituted derivatives, m-bromophenoxydimethylsilane, m-dimethylsilylphenoxydimethylsilane, m-dimethylsilylphenol, and bis(m-dimethylsilylphenyl) carbonate, were similarly prepared and purified. When the liquid bis(m-dimethylsilylphenyl) carbonate, which was purified by distillation, was treated with silver nitrate in an attempt to prepare bis(m-hydroxydimethylsilylphenyl) carbonate, substantial siloxane impurities were present in the product oils. Attempts to purify these oils were unsuccessful.

## 2. Synthesis of Siloxanylenediphenol Derivatives

According to Moehs, tetramethyldisiloxanylenedi-p-phenol can be prepared in good yield by the condensation of lithium p-lithiophenoxide with 1,3-dichlorotetramethyldisiloxane (Reference 7). This procedure was followed for the preparation of the bis(trimethylsilyl) esters of hexamethyltrisiloxanylenedi-p-phenol, octamethyltetrasiloxanylenedi-p-phenol, and octamethyltetrasiloxanylenedi-m-phenol. The unpurified phenol from the reaction mixture was treated with hexamethyldisilazane so that the phenol could be purified by distillation as its trimethylsilyl ester.



Although products were obtained in each of the preparations for which the infrared and nmr spectra confirmed the structure, glc indicated that at best each product was about 80% pure. The extremely high boiling esters could not be further purified by distillation. An alternate approach through the Grignard reagent of the trimethylsilyl-blocked bromophenol provided little or no product.

## SECTION III

## SUMMARY

A summary of the monomers and intermediates prepared and their properties is provided in Table 1.

TABLE 1

SUMMARY OF MONOMERS AND INTERMEDIATES

<u>Name</u>	<u>Melting Point</u> <u>(°C)</u>	<u>Boiling Point</u> <u>[°C (mm)]</u>	<u>20</u> <u>n<sub>D</sub></u>
<u>p</u> -Bromophenoxydimethylsilane	-	83 to 84 (4)	1.5242
<u>p</u> -Dimethylsilylphenoxydimethylsilane	-	74 to 75 (2)	1.4921
<u>p</u> -Dimethylsilylphenol	57 to 58	-	-
Bis( <u>p</u> -dimethylsilylphenyl) carbonate	71 to 72	-	-
Bis( <u>p</u> -hydroxydimethylsilylphenyl) carbonate	95 to 97	-	-
Bis( <u>p</u> -tetramethyldisiloxanylphenyl) carbonate	38 to 39	173 (0.1)	-
Diacetoxydimethylsilane	-	57 to 58 (7)	1.4019
<u>m</u> -Bromophenoxydimethylsilane	-	77 to 78 (4)	1.5228
<u>m</u> -Chlorophenoxydimethylsilane	-	70 to 72 (4)	1.5030
<u>m</u> -Dimethylsilylphenoxydimethylsilane	-	67 to 69 (2)	1.4892
<u>m</u> -Dimethylsilylphenol	-	-	-
Bis( <u>m</u> -dimethylsilylphenyl) carbonate	-	143 to 144 (0.1)	1.5340
Hexamethyltrisiloxanylene-di- <u>p</u> -phenol, bistrimethylsilyl ester (impure)	-	155 to 157 (0.05)	1.4848
Octamethyltetrasiloxanylene-di- <u>p</u> -phenol, bistrimethylsilyl ester (impure)	-	181 to 185 (0.03)	1.4745
Octamethyltetrasiloxanylene-di- <u>m</u> -phenol, bistrimethylsilyl ester (impure)	-	182 to 183 (0.03)	1.4649

## SECTION IV

### EXPERIMENTAL

#### 1. p-Bromophenoxydimethylsilane

A solution of 173 g (1.0 mole) of *p*-bromophenol and 101 g (1.0 mole) of triethylamine in 1,200 ml of petroleum ether, b.p. 35 to 60°, was treated by dropwise addition over a period of 30 min with 94.5 g (1.0 mole) of chlorodimethylsilane. During the addition, the mixture was cooled with a water bath maintained at 20 to 22°. After the mixture was stirred an additional hour, the salts were filtered off and washed with 1,700 ml of petroleum ether. Concentration of the filtrate on a rotary evaporator and fractional distillation of the residue gave 172 g (74%) of *p*-bromophenoxydimethylsilane, b.p. 83 to 84° (4 mm),  $n_D^{20}$  1.5242, infrared spectrum, Figure 1 [Lit. b.p. 78 to 79° (4 mm),  $n_D^{20}$  1.5271 (Reference 8)]. A total of 3,036 g of this compound was prepared by this procedure, but not necessarily on the same scale, in an average yield of 70%.

#### 2. p-Dimethylsilylphenoxydimethylsilane

To 23.4 g (0.96 g atoms) of magnesium was added 75 ml of a solution of 202 g (0.87 mole) of *p*-bromophenoxydimethylsilane in 685 ml of tetrahydrofuran. After the magnesium was activated with a crystal of iodine, the remaining solution was added over a 70-min period at a rate which sustained the exothermic reaction. When the addition was complete, the mixture was stirred and heated to maintain boiling for 6 hr, cooled in an ice-water bath, and treated with 82.7 g (0.874 mole) of chlorodimethylsilane in 15 min. The following day, the salts were filtered off and washed thoroughly with 1,200 ml of petroleum ether, b.p. 60 to 90°. The combined filtrate and washings were concentrated on a rotary evaporator, and the residue was fractionally distilled to obtain 102 g (56%) of *p*-dimethylsilylphenoxydimethylsilane, b.p. 74 to 75° (2 mm),  $n_D^{20}$  1.4921, infrared spectrum, Figure 2 [Lit. b.p. 51° (0.4 mm),  $n_D^{20}$  1.4906 (Reference 3)]. Repetition of this procedure on various size scales gave 1,793 g of the compound in an average yield of 64%. In some preparations, yields were improved through extraction of the distillation residue with petroleum ether and distilling the extract.

#### 3. p-Dimethylsilylphenol

A solution of 126 g (0.60 mole) of *p*-dimethylsilylphenoxydimethylsilane in 240 ml of methanol was mixed with 36 ml of distilled water and stored overnight. Dilution of the solution with 900 ml of water separated an organic phase, which was washed with three 300-ml portions of distilled water and decanted into an evaporating dish. The oil crystallized when stored for 6.5



hr with occasional stirring to provide 85 g (93%) of *p*-dimethylsilylphenol, m.p. 57 to 58°, infrared spectrum, Figure 3, nmr peaks (CCl<sub>4</sub>) at  $\tau$  9.79 (6H doublet  $J = 2$  cps, SiCH<sub>3</sub>),  $\tau$  5.62 (1H septuplet, SiH),  $\tau$  4.03 (1H singlet, OH), and  $\tau$  3.95 (4H quadruplet  $J = 29$  cps, C<sub>6</sub>H<sub>4</sub>) [Lit. m.p. 56° (Reference 3)]. A total of 1,059 g of *p*-dimethylsilylphenol was prepared and the average yield was 88%, not including one preparation in which the phenol rearranged. In some preparations, less pure samples of *p*-dimethylsilylphenoxydimethylsilane were used and lower conversions were obtained.

#### 4. Bis(*p*-dimethylsilylphenyl) Carbonate

To a solution of 110 g (0.73 mole) of *p*-dimethylsilylphenol and 73.6 g (0.73 mole) of triethylamine in 550 ml of toluene and 550 ml of petroleum ether, b.p. 60 to 90°, was added dropwise a solution of 46.4 g (0.47 mole) of phosgene in 305 g of toluene over a period of 2 hr while the mixture was cooled with a 20° water bath. After the mixture was stirred for 1 hr, the triethylamine hydrochloride was filtered off, washed with 500 ml of petroleum ether and the combined filtrates and washing were concentrated on a rotary evaporator. In order to remove any remaining triethylamine hydrochloride, the residue was redissolved in 400 ml of petroleum ether and 300 ml of toluene, filtered, and reconcentrated. The residue, dissolved in 300 ml of hot ethanol, was crystallized in an ice-water bath, and the crystals, collected by filtration and washed with 50 ml of cold ethanol, afforded 101 g (84%) of bis(*p*-dimethylsilylphenyl) carbonate, m.p. 71 to 72°, infrared spectrum, Figure 4, nmr peaks (CCl<sub>4</sub>) at  $\tau$  9.75 (6H doublet  $J = 2$  cps, SiCH<sub>3</sub>),  $\tau$  5.57 (1H septuplet, SiH), and  $\tau$  2.61 (4H quadruplet  $J = 16$  cps, C<sub>6</sub>H<sub>4</sub>) [Lit. m.p. 70° (Reference 4)]. A total of 792 g of this compound was obtained in preparations of varying sizes in an average yield of 70%. Yields were low in some preparations because of apparent failure to remove all triethylamine hydrochloride.

#### 5. Bis(*p*-hydroxydimethylsilylphenyl) Carbonate

A mixture of 16.5 g (0.050 mole) of bis(*p*-dimethylsilylphenyl) carbonate, 625 ml of ether, 120 ml of methanol, and 75 ml of distilled water was stirred very rapidly and cooled in an ice-water while air was slowly introduced into the mixtures through a sparger. After 3 ml of 10% aqueous silver nitrate was added dropwise over a period of 5 hr, the organic phase was separated, washed with three 100-ml portions of distilled water, dried over magnesium sulfate, and concentrated on a rotary evaporator. Recrystallization of the residue from 100 ml of petroleum ether, b.p. 60 to 90°, and 80 ml of benzene gave 11.6 g (64%) of bis(*p*-hydroxydimethylsilylphenyl) carbonate, m.p. 95 to 97°. After the first recrystallization, the silanol was combined with products of other preparations and recrystallized (20 to 30 g) from a mixture of 200 ml of petroleum ether and 500 ml of benzene. In a series of nine preparations, the average overall yield of purified bis(*p*-hydroxydimethylsilylphenyl) carbonate was 56%. In order to achieve this

conversion, it was necessary to rework recrystallization liquors. A total of 263 g of this compound was prepared and the overall yield was 39%.

The procedure was extremely sensitive to minor changes in experimental protocol, particularly stirring rate and rate of addition of the silver nitrate solution. When a similar procedure was followed under an atmosphere of nitrogen, bis(*p*-dimethylsilylphenyl) carbonate was recovered unchanged after the addition of 7 ml of 10% silver nitrate solution over a 5.5-hr period. The infrared spectrum is shown in Figures 5 and 6, nmr peaks (DMSO) at  $\tau$  9.71 (6H singlet, SiCH<sub>3</sub>),  $\tau$  3.95 (1H singlet, SiOH),  $\tau$  2.99 (2H singlet, unidentified), and  $\tau$  2.38 (4H quadruplet, C<sub>6</sub>H<sub>4</sub>).

6. Bis(*p*-hydroxydimethylsilylphenyl) Carbonate (attempted recovery from partially polymerized material)

After 9.8 g (0.025 mole) of partially polymerized bis(*p*-hydroxydimethylsilylphenyl) carbonate was dissolved in a solution of 10 g of sodium hydroxide in 35 ml of methanol and 4 ml of distilled water and treated slowly with a solution of 10 g of sodium hydroxide in 39 ml of distilled water, the resulting mixture was added slowly to a mixture of 102 g of monobasic potassium phosphate in 500 g of ice and 200 g of distilled water. The resulting mixture, warmed to room temperature and filtered, afforded 0.7 g of an unidentified solid.

7. Bis(*p*-1,1,3,3-tetramethyldisiloxanylphenyl) Carbonate

After a solution of 9.5 g (0.1 mole) of chlorodimethylsilane and 10.1 g (0.1 mole) of triethylamine in 100 ml of petroleum ether, b.p. 35 to 60°, was treated with a solution of 18.1 g (0.05 mole) of bis(*p*-hydroxydimethylsilylphenyl) carbonate in 50 ml of dry ether by dropwise addition over a period of 15 min, the salts were filtered off and washed with 140 ml of petroleum ether. The combined filtrate and washing were concentrated on a rotary evaporator, and the residue, fractionally distilled, afforded 17.4 g (73%) of bis(*p*-1,1,3,3-tetramethyldisiloxanylphenyl) carbonate, b.p. 173° (0.1 mm), m.p. 38 to 39°, infrared spectrum, Figure 7. A total of 48.8 g of this compound were prepared in an average yield of 71%.

8. Diacetoxymethylsilane

A solution of 79 g of pyridine in 900 ml of anhydrous ether was treated sequentially with 64.5 g (0.50 mole) of dichlorodimethylsilane and 60 g (1.0 mole) of glacial acetic acid dissolved in 50 ml of ether at room temperature over a period of 1 hr. After the mixture was stirred an additional hour, the pyridine hydrochloride was filtered off and the ether was distilled

away at atmospheric pressure. Fractional distillation of the residue gave 50 g (57%) of diacetoxymethylsilylsilane, b.p. 57 to 58° (7 mm),  $n_D^{20}$  1.4019, infrared spectrum, Figure 8. [Lit. b.p. 54 to 56° (7 mm) (Reference 9.)]

9. Bis(p-1-acetoxy-1,1,3,3-tetramethyldisiloxanylphenyl) Carbonate (attempted)

A mixture of 11.6 g (0.066 mole) of diacetoxymethylsilylsilane and 11.9 (0.033 mole) of bis(p-hydroxymethylsilylphenyl) carbonate was heated at 150° until acetic acid no longer distilled. The residue did not distill when it was heated at 220° (0.05 mm). The infrared spectrum of the residue is shown in Figure 9.

10. Bis(p-methoxymethylsilylphenyl) Carbonate (attempted)

A mixture of 16.5 g (0.050 mole) of bis(p-dimethylsilylphenyl) carbonate, 6.4 mg of chloroplatinic acid hexahydrate, and 400 ml of dry methanol was heated at boiling for 1 hr, cooled, and concentrated on a rotary evaporator. The residue, dissolved in 100 ml of hot petroleum ether, b.p. 35 to 60°, treated with charcoal, filtered, and concentrated, gave a residue with strong Si<sub>2</sub>O absorption at 1090 cm<sup>-1</sup> in its infrared spectrum (Figure 10).

11. m-Bromophenoxydimethylsilylsilane

In a procedure similar to the method for preparing p-bromophenoxydimethylsilylsilane, 173 g (1.0 mole) of m-bromophenol, 101 g (1.0 mole) of triethylamine, and 95.6 g (1.0 mole) of chlorodimethylsilylsilane gave 144 g (62%) of m-bromophenoxydimethylsilylsilane, b.p. 77 to 78°,  $n_D^{20}$  1.5228, infrared spectrum, Figure 11. A total of 466 g of this compound was obtained from various sized preparations with an average yield of 64%.

12. m-Chlorophenoxydimethylsilylsilane

When 100 g (0.78 mole) of m-chlorophenol was treated with 73.5 g (0.78 mole) of chlorodimethylsilylsilane and 78.6 g (0.78 mole) of triethylamine in the manner described for the synthesis of p-bromophenoxydimethylsilylsilane and the product was fractionally distilled, 80.0 g (57%) of m-chlorophenoxydimethylsilylsilane, b.p. 70 to 72° (4 mm),  $n_D^{20}$  1.5030, infrared spectrum, Figure 12, was obtained.

13. m-Dimethylsilylphenoxydimethylsilane

The procedure for the synthesis of p-dimethylsilylphenoxydimethylsilane, applied to the preparation of this compound, gave 149 g (57%) of m-dimethylsilylphenoxydimethylsilane, b.p. 67 to 69° (2 mm),  $n_D^{20}$  1.4892, from 114 g (0.62 mole) of m-bromophenoxydimethylsilane, 16.6 g (0.68 g atom) of magnesium, and 58.8 g (0.62 mole) of chlorodimethylsilane. A total of 229 g of this compound was prepared and the average yield was 55%. The infrared spectrum of this compound is shown in Figure 13, nmr peaks (CCl<sub>4</sub>) at  $\tau$  9.78 (6H doublet  $J = 2$  cps,  $\text{HSi}(\text{CH}_3)_2\text{C}_6\text{H}_4$ ),  $\tau$  9.74 (6H doublet  $J = 2$  cps,  $\text{HSi}(\text{CH}_3)_2\text{O}$ ),  $\tau$  5.57 (1H septuplet,  $\text{HSi}(\text{CH}_3)_2\text{C}_6\text{H}_4$ ),  $\tau$  4.99 (1H septuplet,  $\text{HSi}(\text{CH}_3)_2\text{O}$ ), and  $\tau$  2.68 to 3.25 (4H multiplet,  $\text{C}_6\text{H}_4$ ).

14. m-Dimethylsilylphenol

When 111 g (0.53 mole) of m-dimethylsilylphenoxydimethylsilane was treated in a manner described for the preparation of p-dimethylsilylphenol, 68 g (85%) of m-dimethylsilylphenol,  $n_D^{20}$  1.5270, infrared spectrum Figure 14, nmr peaks (CCl<sub>4</sub>) at  $\tau$  9.79 (6H doublet  $J = 2$  cps,  $\text{SiCH}_3$ ),  $\tau$  5.67 (1H septuplet,  $\text{SiH}$ ),  $\tau$  3.87 (1H singlet, OH), and  $\tau$  2.77 to 3.29 (4H multiplet,  $\text{C}_6\text{H}_4$ ) was obtained. A total of 153 g of this compound was prepared and the average yield was 80%.

15. Bis(m-dimethylsilylphenyl) Carbonate

The procedure employed for the preparation of bis(p-dimethylsilylphenyl) carbonate was followed in treating 120 g (0.79 mole) of m-dimethylsilylphenol with 79.6 g (0.79 mole) of triethylamine and 55.6 g (0.56 mole) of phosgene. Fractional distillation of the unpurified product afforded 111 g (86%) of bis(m-dimethylsilylphenyl) carbonate, b.p. 143 to 144° (0.12 mm),  $n_D^{20}$  1.5340, infrared spectrum Figure 15, nmr peaks (CCl<sub>4</sub>) at  $\tau$  9.70 (6H doublet  $J = 2$  cps,  $\text{SiCH}_3$ ),  $\tau$  5.55 (septuplet,  $\text{SiH}$ ), and  $\tau$  2.59 to 2.77 (4H multiplet,  $\text{C}_6\text{H}_4$ ). An additional 27 g (86%) of this compound was obtained in a second preparation.

16. Bis(m-hydroxydimethylsilylphenyl) Carbonate (attempted)

An attempt to prepare the subject compound by the procedure described for the synthesis of bis(p-hydroxydimethylsilylphenyl) carbonate from 16.5 g (0.05 mole) of bis(m-dimethylsilylphenyl) carbonate treated with 11 ml of 10% silver nitration solution over a period of 6.5 hr failed to give a product that could be crystallized from benzene or benzene-petroleum ether mixtures. The infrared spectrum of the product contained a strong siloxane absorption in the 1020 to 1100  $\text{cm}^{-1}$  region.

17. 1,1,3,3,5,5-Hexamethyltrisiloxanylenedi-p-phenol, (Bistrimethylsilyl Ester  
(via the organolithium intermediate)

A solution of 50.9 g (0.80 mole) of *n*-butyllithium in hexane (477 ml of a 15% solution) was cooled in an isopropyl alcohol-dry ice bath to  $-50^{\circ}$  and a solution of 57.7 g (0.33 mole) of *p*-bromophenol in 800 ml of tetrahydrofuran over 1.75 hr while the temperature was maintained below  $-50^{\circ}$ . The solution was subsequently allowed to warm to 0 to  $5^{\circ}$  and stirred at that temperature for 40 min. During the warming, gelation occurred at about  $-20^{\circ}$ . The mixture was again cooled to  $-60^{\circ}$  and treated with a solution of 27.7 g (0.1 mole) of 1,5-dichlorohexamethyltrisiloxane. After the addition was complete, the mixture was allowed to warm to  $0^{\circ}$ , was stirred an additional hour, and was treated with 100 ml of saturated aqueous ammonium chloride solution. The organic phase, separated and combined with two 100-ml ethyl ether washings of the aqueous phase, was concentrated on a rotary evaporator, and the residue was dissolved in ether and extracted with water until no more color was removed. After the ether solution was reconcentrated, the residue was heated in a solution of 32 g (0.2 mole) of hexamethyldisilazane in 100 ml of petroleum ether, b.p. 60 to  $90^{\circ}$ . When the product was concentrated and fractionally distilled, the following fractions were obtained: (a) 3.9 g, boiling at 161 to  $175^{\circ}$  (0.1 mm); (b) 3.5 g, boiling at 176 to  $185^{\circ}$  (0.1 mm); and (c) 15.2 g, boiling at 188 to  $200^{\circ}$  (0.1 mm). Redistillation of fraction (c) gave 14.5 g (36%) of impure bistrimethylsilyl ester of hexamethyltrisiloxanylenedi-*p*-phenol, b.p. 155 to  $157^{\circ}$  (0.05 mm),  $n_D^{20}$  1.4848 infrared spectrum, Figure 16, nmr peaks ( $CCl_4$ ) at  $\tau$  9.95 (6H singlet,  $OSi(CH_3)_2O$ ),  $\tau$  9.78 and 9.73 (39H, 2 singlets,  $Si(CH_3)_3$  and  $C_6H_4Si(CH_3)_2$ ), and  $\tau$  2.90 (8H quadruplet,  $C_6H_4$ ). The glc purity of the sample was about 77% and it contained about seven components (column packed with OV-1 on 80/100 Supelcoport, 100 to  $250^{\circ}$  at  $10^{\circ}/min$ , N carrier at 70 cc/min).

18. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxanylenedi-p-phenol, Bistrimethylsilyl Ester

By a procedure similar to the preparation of hexamethyltrisiloxanylenedi-*p*-phenol, bistrimethylsilyl ester, via the organolithium intermediate, the product from 57.7 g (0.33 mole) of *p*-bromophenol and 53.3 g (0.83 mole) of *n*-butyllithium in hexane (500 ml of a 15% solution) in 800 ml of tetrahydrofuran was treated with 35.1 g (0.10 mole) of 1,7-dichlorooctamethyltetrasiloxane and subsequently with 32.2 g (0.20 mole) of hexamethyldisilazane. Fractional distillation gave the following: 15.1 g, boiling at 172 to  $179^{\circ}$  (0.08 mm); and 1.4 g boiling at 180 to  $184^{\circ}$  (0.1 mm). Redistillation of the two fractions gave 11.8 g (19%) of the bis trimethylsilyl ester of octamethyltetrasiloxanylenedi-*p*-phenol, b.p. 181 to  $185^{\circ}$  (0.03 mm),  $n_D^{20}$  1.4745, infrared spectrum, Figure 17, nmr peaks ( $CCl_4$ ) at

$\tau$  9.99 (6H singlet,  $\text{OSi}(\text{CH}_3)_2\text{O}$ ),  $\tau$  9.75 (6H singlet,  $\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{O}$ ),  $\tau$  9.71 (9H singlet,  $\text{Si}(\text{CH}_3)_3$ , and  $\tau$  2.94 (4H quadruplet,  $\text{C}_6\text{H}_4$ ). The glc purity of the sample was about 83% and it contained about 10 components (column packed with 3% OV-1 on 80/100 Supelcoport, 100 to 250° at 10°/min, N carrier at 70 cc/min).

19. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxanylenedi-m-phenol, Bistrimethylsilyl Ester

In manner similar to the preparation of hexamethyltrisiloxanylenedi-p-phenol, 57.7 g (0.33 mole) of m-bromophenol, treated with 45.4 g (0.71 mole) of n-butyllithium in hexane (2.29 molar), was condensed with 35.1 g (0.1 mole) of 1,7-dichlorooctamethyltetrasiloxane. The product was heated with 32.2 g (0.2 mole) of hexamethyldisilazane and prepared for distillation. Fractional distillation gave (a) 3.1 g boiling at 160 to 164° (0.03 mm); (b) 6.2 g, boiling at 170 to 180° (0.03 mm); and (c) 2.3 g, boiling at 182 to 183° (0.03 mm). The yield of octamethyltetrasiloxanylenedi-m-phenol, bistrimethylsilyl ester, represented by fractions (b) and (c) was 13%. The refractive index of fraction (c) was  $n_D^{20}$  1.4649, infrared spectrum, Figure 18.

20. p-Bromophenoxytrimethylsilane

After a solution of 173 g (1.0 mole) of p-bromophenol and 80.5 g (0.5 mole) of hexamethyldisilazane in 500 ml of petroleum ether, b.p. 60 to 90°, was refluxed for 2 hr, the solution was concentrated on a rotary evaporator and fractionally distilled to obtain 230 g (94%) of p-bromophenoxytrimethylsilane, b.p. 123° (21 mm),  $n_D^{20}$  1.5183, infrared spectrum, Figure 19 [Lit. b.p. 122° (20 mm) (Reference 2)].

21. m-Bromophenoxytrimethylsilane

With a procedure similar to the method for preparing p-bromophenoxytrimethylsilane, 100 g (0.58 mole) of m-bromophenol and 47 g (0.29 mole) of hexamethyldisilazane in 300 ml of petroleum ether, b.p. 60 to 90°, gave 123 g (86%) of m-bromophenoxytrimethylsilane, b.p. 115 to 116° (20 mm),  $n_D^{20}$  1.5160, infrared spectrum, Figure 20.



22. 1,1,3,3,5,5-Hexamethyltrisiloxanylenedi-p-phenol, Bis(trimethylsilyl)  
Ester (attempted via the Grignard method)

A solution of 48.9 g (0.2 mole) of p-bromophenoxytrimethylsilane in 155 ml of tetrahydrofuran was added to 5.3 g (0.22 g atom) of previously activated magnesium at a rate that maintained reflux. After the mixture was heated and stirred for 3 hr, it was cooled in an ice-water bath and treated with 20.7 g (0.075 mole) of 1,5-dichlorohexamethyltrisiloxane. Heating was continued for 2 hr, and subsequently the salts were filtered off and washed with petroleum ether. After the combined washings and filtrate were concentrated on a rotary evaporator, the residue was extracted with two 200-ml portions of petroleum ether, and the extracts were filtered and reconcentrated. Distillation gave 8.3 g of material, boiling at 101 to 188° (0.2 mm). In a repetition of the procedure 5.1 g of material, boiling at 107 to 221° (0.2 mm) was obtained. When the two distillates were combined and fractionally distilled, the following fractions were obtained: (a) 2.7 g, boiling to 148° (0.2 mm); (b) 6.5 g, boiling at 156 to 200° (0.2 mm); (c) 2.4 g, boiling at 209 to 221° (0.2 mm); and (d) 0.8 g, boiling at 224 to 236° (0.2 mm). The infrared spectrum of fraction (b) is shown in Figure 21.

23. Samples

The following samples were forwarded to Wright-Patterson Air Force Base: (a) bis(p-hydroxydimethylsilylphenyl) carbonate, 155.7 g, m.p. 96 to 97°; (b) bis(p-1,1,3,3-tetramethyldisiloxanylphenyl) carbonate, 48.8 g, m.p. 38 to 39°.



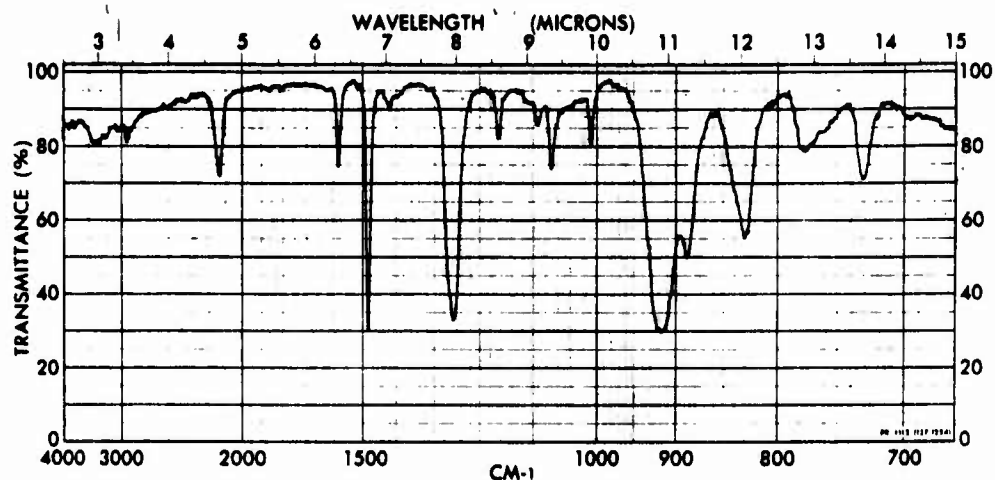


Figure 1 - Infrared Spectrum of *p*-Bromophenyldimethylsilane (Film)

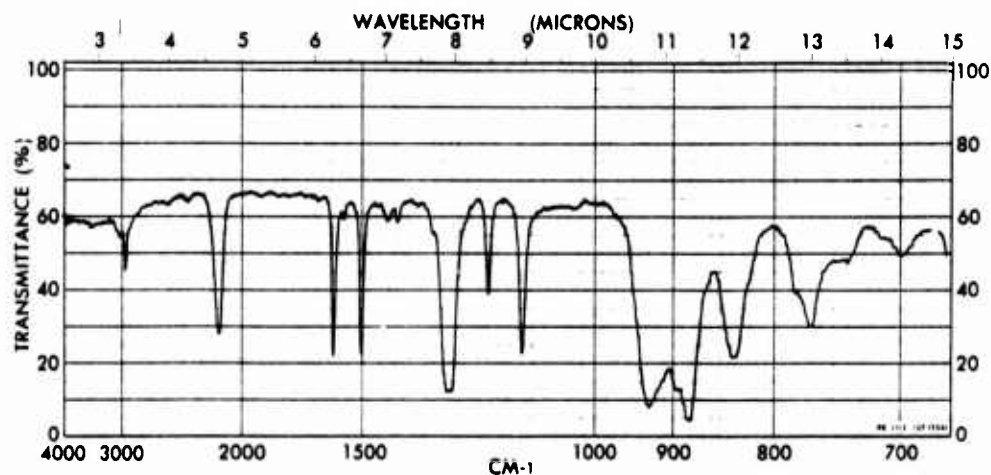


Figure 2 - Infrared Spectrum of *p*-Dimethylsilylphenoxydimethylsilane (Film)

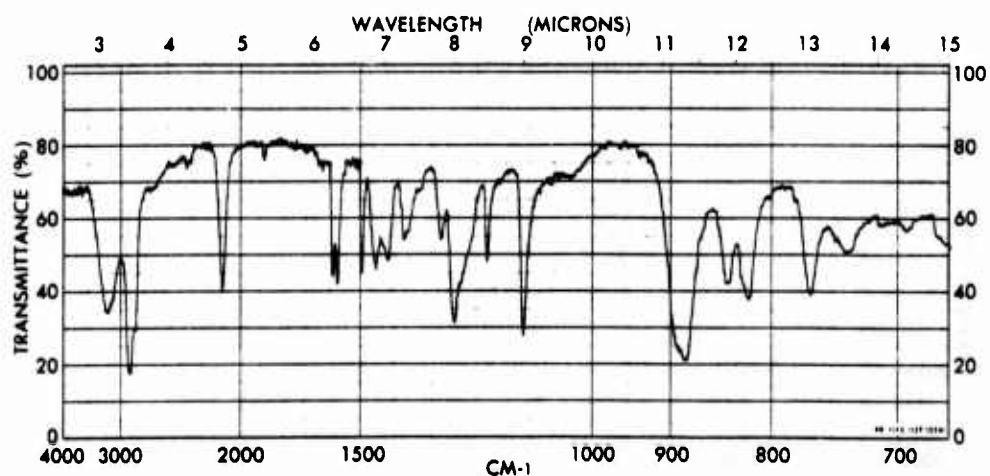


Figure 3 - Infrared Spectrum of *p*-Dimethylsilylphenol (Nujol)

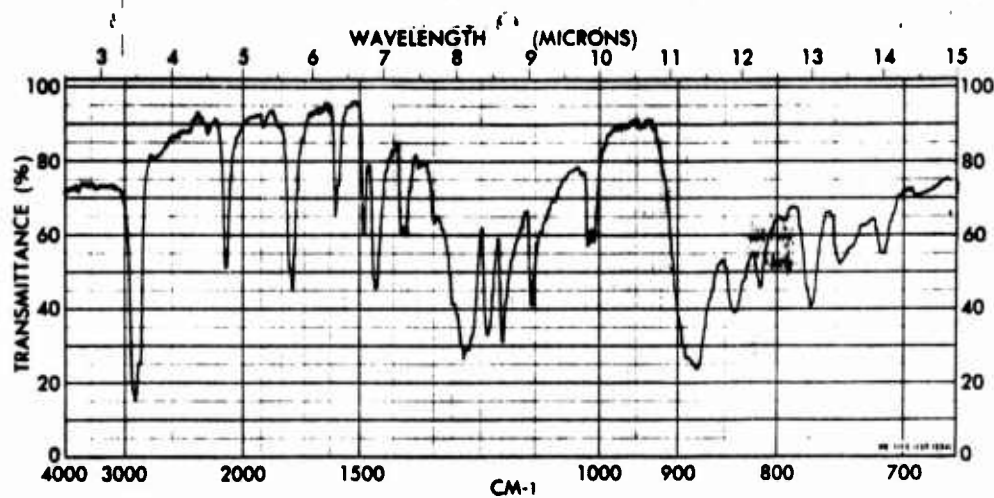


Figure 4 - Infrared Spectrum of Bis(p-dimethylsilylphenyl) Carbonate (Nujol)

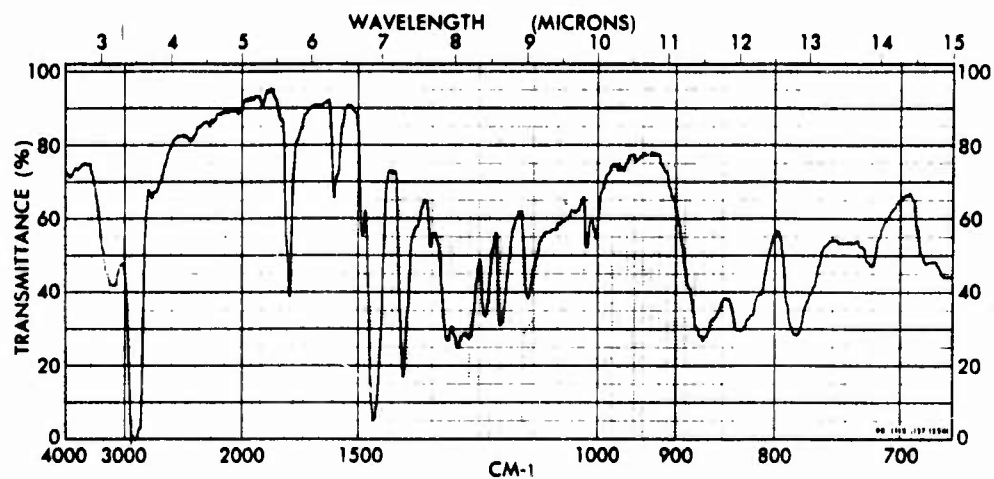


Figure 5 - Infrared Spectrum of Bis(p-hydroxydimethylsilylphenyl) Carbonate (Nujol)

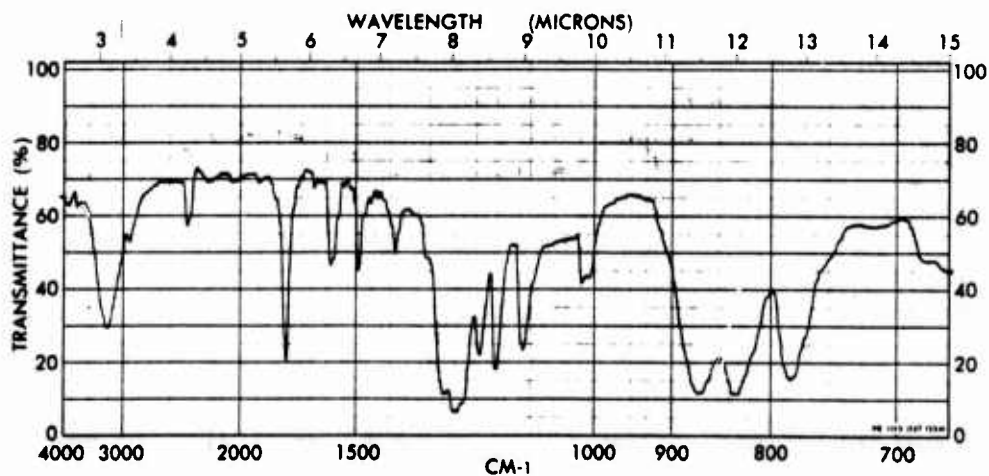


Figure 6 - Infrared Spectrum of Bis(p-hydroxydimethylsilylphenyl) Carbonate (KBr)

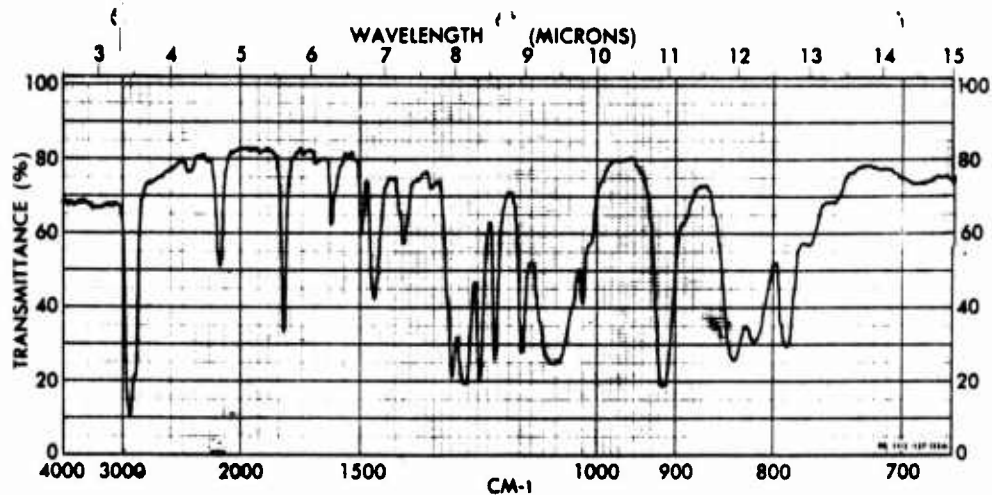


Figure 7 - Infrared Spectrum of Bis(p-tetramethyldisiloxanylphenyl) Carbonate (Nujol)

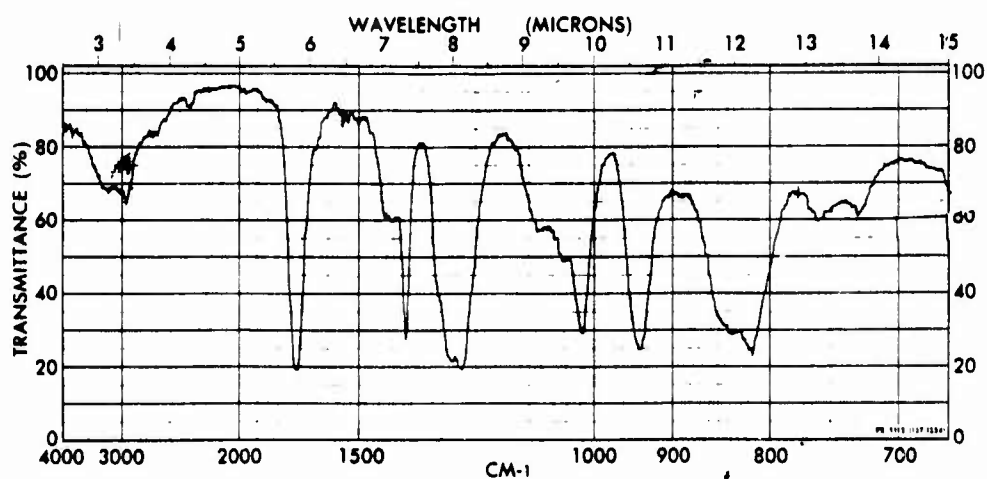


Figure 8 - Infrared Spectrum of Diacetoxymethylsilane (Film)

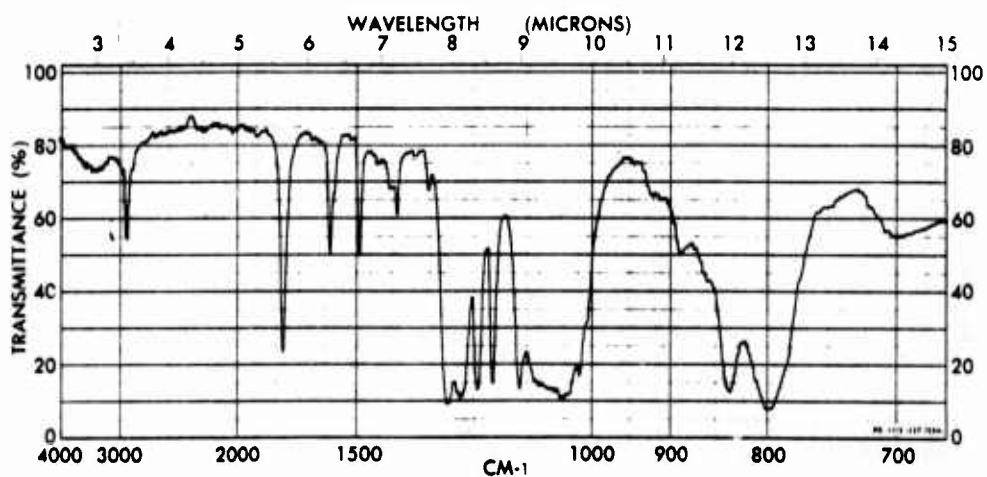


Figure 9 - Infrared Spectrum of the Condensation Product of Diacetoxymethylsilane and Bis(p-hydroxydimethylsilylphenyl) Carbonate (Film)

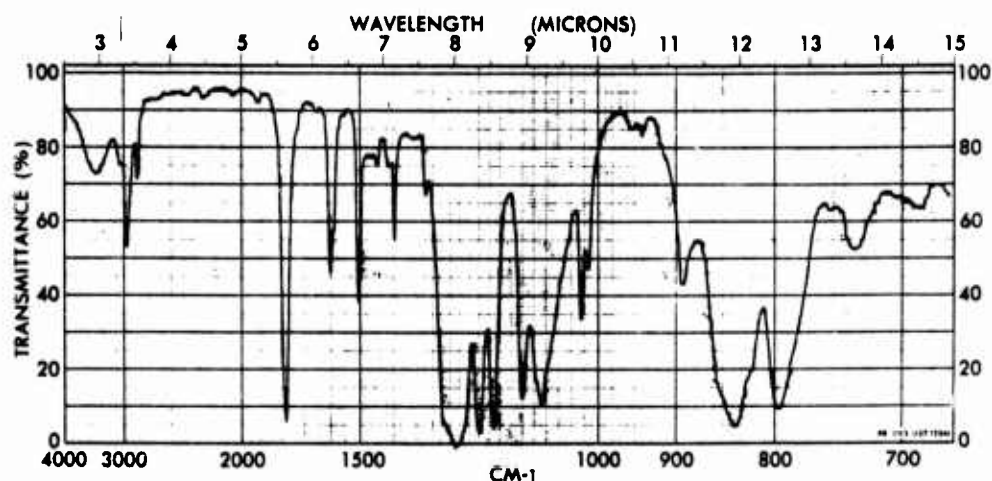


Figure 10 - Infrared Spectrum of the Product of Treating Bis(p-dimethylsilylphenyl) Carbonate with Methanol and Chloroplatinic Acid (Film)

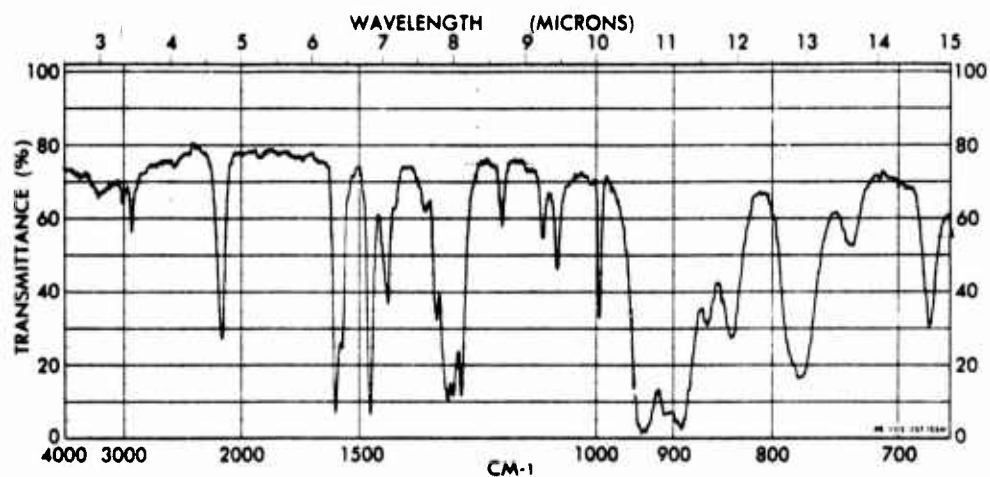


Figure 11 - Infrared Spectrum of m-Bromophenyloxydimethylsilane (Film)

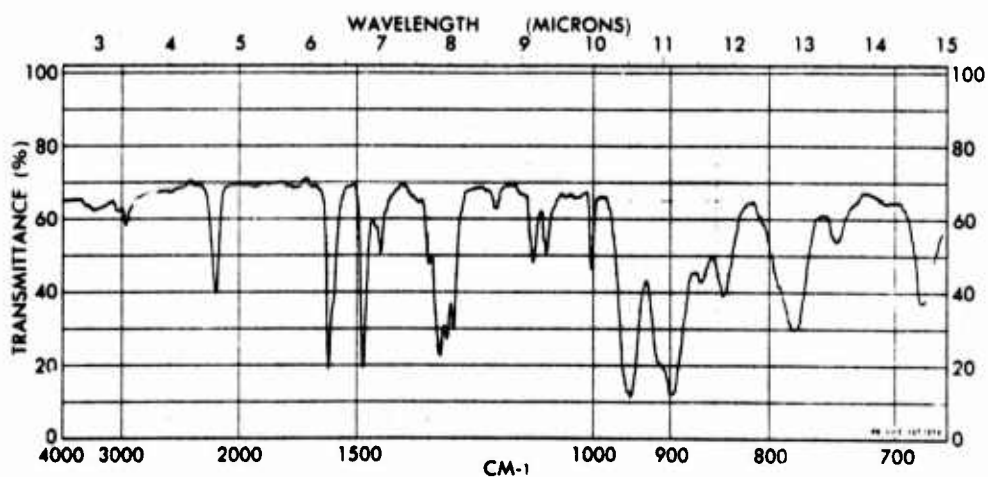


Figure 12 - Infrared Spectrum of m-Chlorophenyloxydimethylsilane (Film)

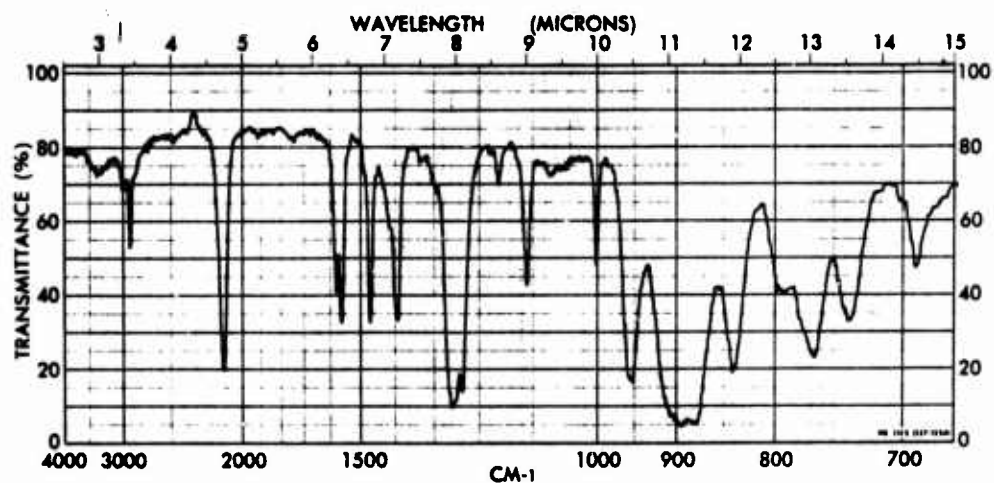


Figure 13 - Infrared Spectrum of m-Dimethylsilylphenoxymethylsilane (Film)

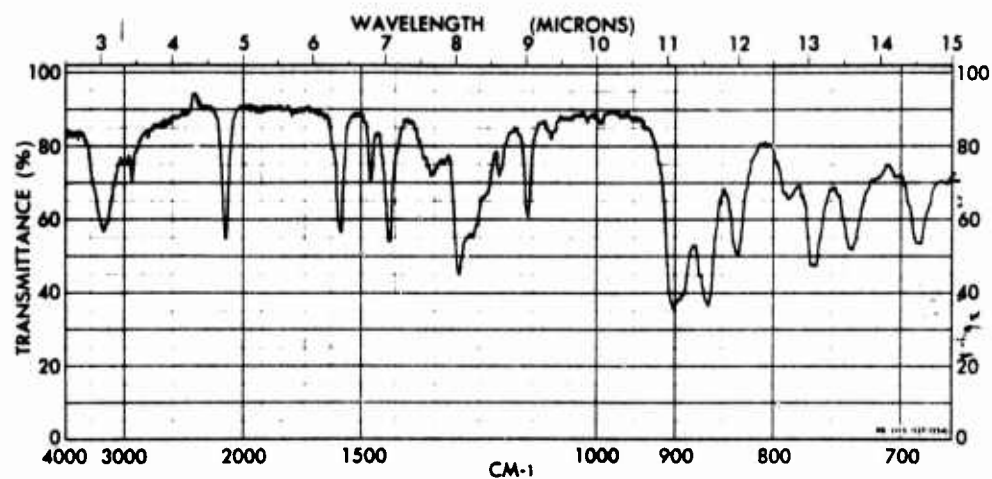


Figure 14 - Infrared Spectrum of m-Dimethylsilylphenol (Film)

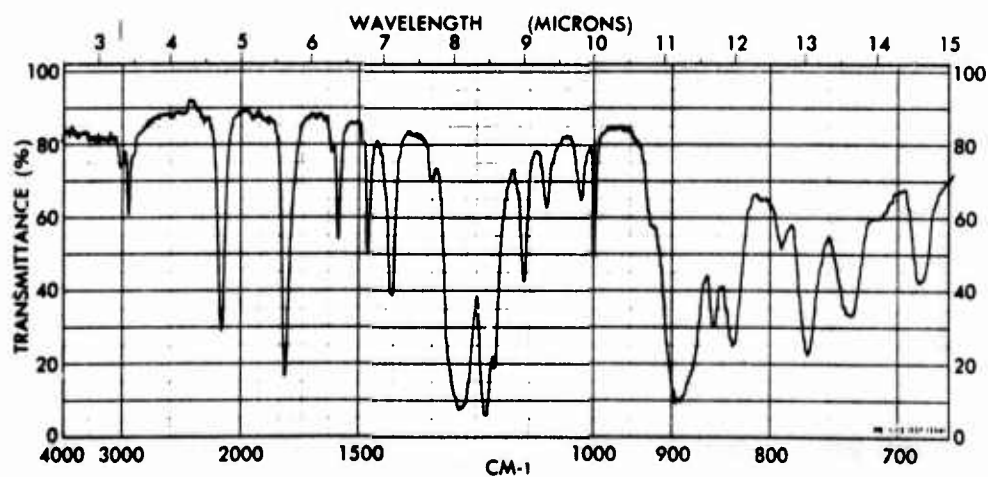


Figure 15 - Infrared Spectrum of Bis(m-dimethylsilylphenyl) Carbonate (Film)



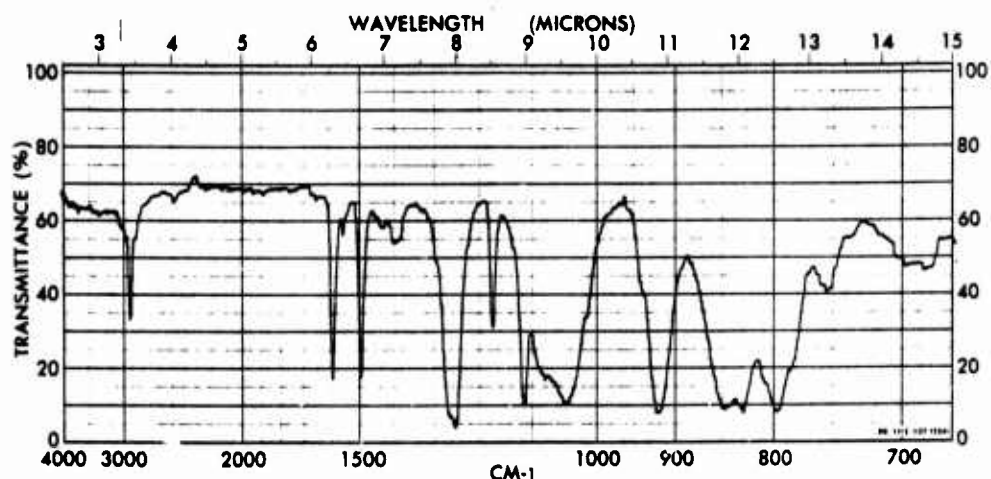


Figure 16 - Infrared Spectrum of Hexamethyltrisiloxanylenedi-  
p-phenol, Bistrimethylsilyl Ester (Film)

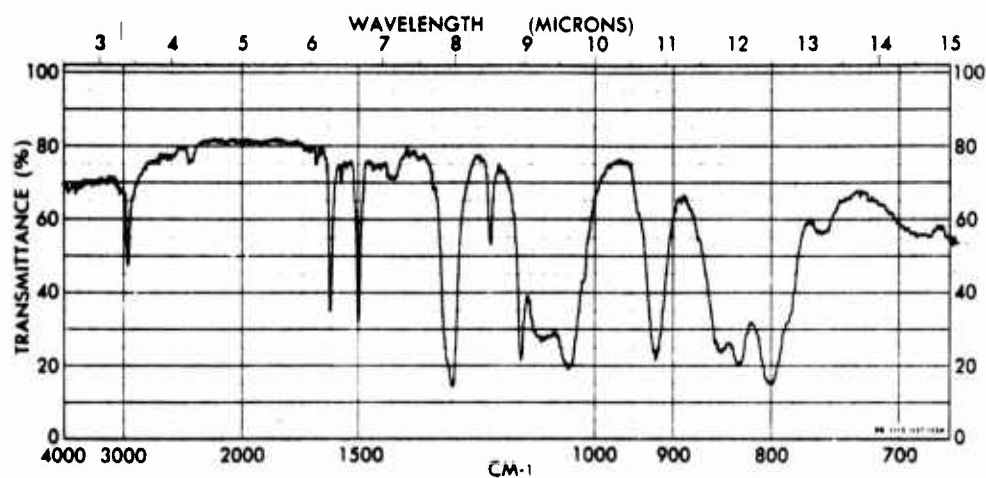


Figure 17 - Infrared Spectrum of Octamethyltetrasiloxanylenedi-  
p-phenol, Bistrimethylsilyl Ester (Film)

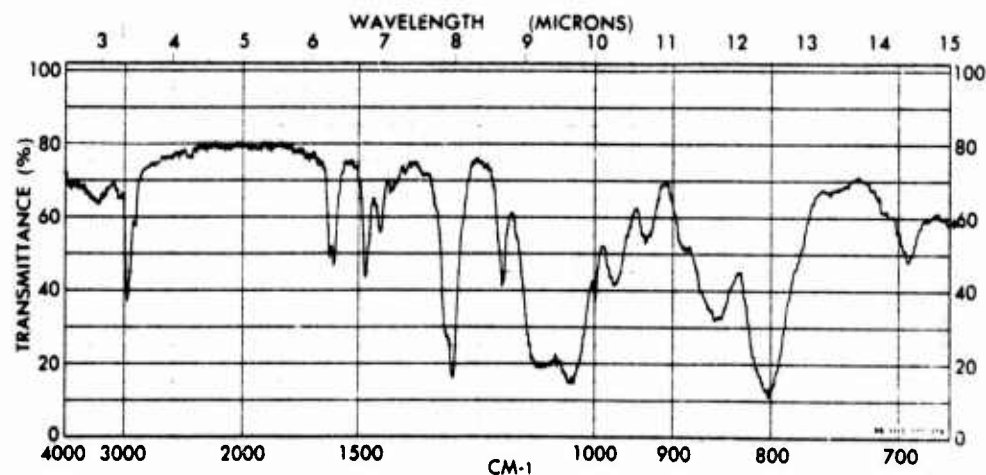


Figure 18 - Infrared Spectrum of Octamethyltetrasiloxanylene-  
di-m-phenol, Bistrimethylsilyl Ester (Film)

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